Title
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Scope of the Project

The goal of this program is to extend fundamental knowledge of combustion processes by theoretical studies of the dynamics of energy transfer, reactive, and photodissociative processes. The approach is based on the reliable description of inter- and intramolecular interactions using ab initio methods and a variety of approaches to describe the dynamics of nuclear motion. A summary of recent results and future plans follows.

Recent Results

A) Quantum Monte Carlo Calculation of the Singlet-Triplet Splitting in CH₂

The fixed-node quantum Monte Carlo (FNQMC) method was used to calculate the total energy of CH₂ in the 3B₁ and 1A₁ states. For both states, the best FNQMC variationally bounded energies lie more than 15 kcal/mole below the best previous variational calculations. Subtracting these energies to obtain the singlet-triplet splitting yields Tₑ = 9.4 ± 2.2 kcal/mole and Tₒ = 8.9 ± 2.2 kcal/mole. This result is in excellent agreement with the recent direct measurements of McKellar et al. of Tₒ = 9.05 ± 0.06 kcal/mole, and of Leopold et al. of -9 kcal/mole, as well as with recent theoretical investigations which indicate an energy gap of 9-11 kcal/mole.

B) FNQMC Study of the Classical Barrier Height for the H + H₂ Exchange Reaction

The classical barrier height for the H + H₂ exchange reaction, as well as the energies at two other points along the reaction path, were calculated using the FNQMC method. The computed barrier is an upper bound since the energy of H and of H₂ is obtained exactly by FNQMC. Our best upper bound, 9.70 ± 0.13 kcal/mole, has a mean within 0.1 kcal/mole of the presumed exact value.

C) Ab Initio Study of Ground and Excited States of Cyanogen

An ab initio MCHF study of the X 1Σ⁺, A 3Σ⁺, B 1Δᵥ, and C 1Πᵥ states of cyanogen (C₂N₂) was carried out to provide input data for our adiabatic theory of photodissociation and to yield new information on the properties of these states. Equilibrium structures, harmonic vibrational frequencies, excitation energies, and dissociation energies were calculated and found to be in semi-quantitative agreement with...
available experimental data, where available. This study confirmed the \( \pi \rightarrow \pi^* \) character of \( \text{C}_2\text{N}_2 \left( \text{A}^2\Sigma_u^+ \right) \) and \( \text{C}_2\text{N}_2 \left( \text{B}^1\Delta_u \right) \), and the \( \pi \rightarrow \pi^* \)
character of \( \text{C}_2\text{N}_2 \left( \text{C}^1\Pi_u \right) \) in each case near the equilibrium structure. For \( \text{C}_2\text{N}_2 \left( \text{A}^2\Sigma_u^+ \right) \) and \( \text{C}_2\text{N}_2 \left( \text{B}^1\Delta_u \right) \), the harmonic force constants show a strong through-bond interaction which is due to the dominance of the charge transfer configuration \( ^{1}\text{NCCN}^- \).

D) Theoretical Study of the \( \text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}_2 \rightarrow \text{HO}_2 \) System
(joint with H. F. Schaefer, III)

\( \text{Ab initio} \) MCHF calculations were carried out to characterize the \( \text{H}(2\text{S}) + \text{O}_3(1\text{A}_1) \) potential energy surface (pes). It was found that the \( \text{H} \) atom approaches a terminal O of \( \text{O}_3 \) from above the plane of the molecule to form the \( \text{HO}_3 \) intermediate, which then undergoes fragmentation. No planar transition state connecting \( \text{H} + \text{O}_3 \) to \( \text{OH} + \text{O}_2 \) was found. Instead, inplane approach of the \( \text{H} \) atom leads to \( \text{H} + \text{O} + \text{O}_2 \). No energy barrier to formation of \( \text{HO}_3 \) was found for \( \text{HO}_2 + \text{O} \). H atom abstraction, however, was found to have a small activation energy. These findings are consistent with the observed formation of vibrationally excited \( \text{OH} \) product.

E) Rotational Excitation of \( \text{H}_2(\text{B}^1\Sigma_u^+) \) by He Impact

Using \( \text{ab initio} \) SCF-CI methods combined with earlier \( \text{ab initio} \) data of comparable quality, the potential energy surface (pes) for the subject system has been determined over a sufficient range of nuclear coordinates to determine an analytical fit useful for coupled-channel scattering calculations. The pes is found to be highly anisotropic, unlike the corresponding ground-state surface, because of crossings with surfaces that correlate at long range with \( \text{H}_2(\text{B}^1\Sigma_u^+) \) and ground state \( \text{H}_2 \). Cross sections for rotational energy transfer are consequently larger than those previously obtained for ground-state neutral atom-diatom systems.

Future Plans

A) Electron Affinity of Fluorine

A FNQMC study has been very recently initiated as a part of our effort to ascertain the capability of the method to provide a variety of molecular properties.

B) Rovibrational Energy Transfer and Electronic Quenching in
\( \text{H}_2(\text{B}^1\Sigma_u^+) - \text{He}(1\text{S}) \)

The study of rotational excitation will be extended to the two processes indicated to enable cross section comparisons with earlier measurements.

C) Adiabatic Theory of Photodissociation and Chemical Reactions

Both directions will be pursued. Our present indirect photodissociation study of \( \text{C}_2\text{N}_2 \) in the collinear model will be extended to three-dimensions (3D) and our collinear model for chemical reaction will be applied to systems with arbitrary mass combinations and subsequently, extended to 3D.
Publications


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